Alexandria Engineering Journal (2014) 53, 205–211

Alexandria University

Alexandria Engineering Journal

www.elsevier.com/locate/aej
www.sciencedirect.com

REVIEW

Treatment of wastewater contaminated with cobalt using Saudi activated bentonite

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Received 26 July 2013; revised 26 October 2013; accepted 30 October 2013
Available online 28 November 2013

KEYWORDS

Cobalt removal;
Saudi bentonite;
Cobalt adsorption;
Heavy metals removal;
Adsorption isotherm

Abstract In this study, removal of cobalt from wastewater using Saudi activated clay (bentonite) was investigated. The removal characteristics were investigated under various operating variables such as contact time, solution pH, clay dosage and initial metal concentration. It was found that adsorption of cobalt ions on Saudi activated bentonite was relatively fast and the equilibrium was reached after 30 min. Adsorption was also dependent on solution pH where cobalt removal percentage gradually increased with increasing solution pH up to 99% at pH 8. Moreover, about 100% cobalt removal was observed when solution pH was increased to more than 8. The results showed that increasing the initial cobalt concentration decreased cobalt removal percentage due to saturation of clay with cobalt ions. The adsorption isotherm data were well fitted with both the linearized Langmuir and Freundlich models. Furthermore, the value of the mean free energy determined with the D–R equation showed that adsorption process is chemisorptions. Cobalt adsorption into Saudi activated bentonite was well represented by the pseudo-second-order kinetic model.

Contents

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Peer review under responsibility of Faculty of Engineering, Alexandria University.

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http://dx.doi.org/10.1016/j.aej.2013.10.006

1. Introduction

This study aims to investigate the feasibility of using Saudi activated clay (bentonite) in removing cobalt from wastewater.

Wastewaters from metal industries contain various toxic heavy metals. These heavy metals present a high health risk when they enter the human food chain [1,2]. Cobalt is a very toxic element affecting the environment. Cobalt is present in the wastewater of nuclear power plants and many other industries such as mining, metallurgical, electroplating, paints, pigments and electronic industries. High levels of cobalt may affect several health problems such as paralysis, diarrhea, low blood pressure, lung irritation and bone defects [3,4]. The standard level of cobalt in drinking water is 2 μg/L [5].

Adsorption of cobalt ions by different types of clay has been the subject of several studies [5–10]. These studies investigate the effect of different factors which affect the adsorption process such as sorbent amount, initial metal-ion concentration, contact time and solution pH.

The khulays bentonite (Saudi bentonite) which is located 95 km north of Jeddah is calcium montmorillonite equivalent to a "Texas bentonite" in the USA or Fuller's earth in the UK. It has reserves ranging from 420 thousand tons (proven) to 28.9 million tons (indicated) and 38.9 million tons (possible) [11].

Saudi activated bentonite was used for the removal of lead from aqueous solutions. The results showed that sorption of lead ions on Saudi activated clay was affected by shaking time, initial lead concentration, and mixture pH. Saudi activated bentonite can be considered as a promising adsorbent for the removal of other heavy metals from aqueous solutions [12].

Therefore, the main objective of this study is to investigate the feasibility of using Saudi activated clay (bentonite) in removing cobalt from wastewater. The choice of this material is based on its low cost, considering its abundance in Khulays bentonite deposit.

2. Experiment

2.1. Materials and method

2.1.1. Chemicals and reagents

Cobalt was obtained from Merck. A 1000 mg/L Stock solution of cobalt was prepared by dissolving the appropriate amounts of cobalt chloride 6-hydrate ($CoCl_2{\cdot}6H_2O$) in distilled water. The stock solutions were diluted as required to obtain standard solutions containing 20–210 mg/L of cobalt. The pH of each experimental solution was adjusted to the required pH value using 1N HCl and 1N NaOH.

2.1.2. Adsorbent

Saudi bentonite was obtained from Khulays bentonite deposit. It was not active in its natural state where some treatment was required to modify its adsorptive property. Saudi bentonite samples were collected as ungrounded rocks where grinding and sieving processes were conducted before acid activation. The apparatus and chemical treatment method with H_2SO_4 that were employed in this study were similar to what was described previously [13–15]. Acid activation was done using the optimum operating variables such as 15% by weight acid concentration, the temperature of boiling, 90 min reaction time, particle size of −200 mesh (74 μm) and water to clay ratio of 5:1. The surface area of Saudi natural clay was improved from 60 to be 299 m^2/g after activation process. Table 1 shows the chemical composition of Saudi Activated bentonite.

2.1.3. Adsorption process

Adsorption of cobalt with clay was carried out using batch adsorption technique. A certain amount of bentonite and 50 mL of cobalt solution at desired initial concentration were added to 100 mL stoppered conical flasks. The flasks were shaken in a horizontal shaker with water bath at 200 rpm. Stock solution (1000 mg/L) of cobalt was prepared by dissolving the appropriate amounts of cobalt chloride in distilled water.

Table 1 Chemical composition of Saudi Activated bentonite [13].

Compound	Chemical composition (%)
SiO_2	66.2
Al_2O_3	11.71
Fe_2O_2	3.0
TiO_2	1.5
MgO	0.73
CaO	< 0.05
K_2O	0.48
Na_2O	0.12
MnO	0.05
SO_3	< 0.05
P_2O_5	< 0.05
L.O.I. (1000 °C)	15.3

The stock solutions were diluted as required to obtain standard solutions containing 20–210 mg/L of cobalt. pH adjustments were carried out using 1N HCl and 1N NaOH. 200 rpm Shaking rate and a temperature of 25 ± 2 °C was applied to the shaker. Samples with clay content in the range of 0.5–1.0 g were taken from the shaker at regular contact time intervals. The sorbent and solution were separated by filtration after each run. The filtrate was analyzed for cobalt concentration by Atomic Absorption Spectrophotometer. The effects of several factors such as solution pH, concentration of solution, clay mass and contact time on cobalt removal efficiency were examined. The obtained data were used to calculate the equilibrium metal uptake capacity according to the following equation:

$$q_e = \frac{V(C_o - C_e)}{m} \quad (1)$$

where C_o is the initial concentration of cobalt ions (mg/L); C_e is equilibrium concentration of cobalt ions (mg/L); q_e is amount of cobalt ions adsorbed per unit weight of adsorbent (mg/g); V is volume of the solution (L); m is the sorbent dose (g).

3. Results and discussions

3.1. Effect of contact time

The effect of contact time on the adsorption of cobalt by Saudi activated bentonite for different initial concentrations can be seen in Fig. 1. The effect of shaking time on cobalt adsorption was investigated by varying the contact time between the adsorbate and adsorbent in the range 2–60 min. The initial concentration of cobalt ranged from 20 to 100 mg/L, while the dose of clay sample was 0.5 g/50 mL of cobalt solution. The pH of the solution was kept unchanged at 3.2. The data showed that the sorption of cobalt ions on Saudi activated bentonite is relatively fast where the equilibrium was achieved after 30 min. The adsorption process was fast at the beginning of the reaction due to the adsorption of cobalt on the surface sites of clay.

The results showed that shaking the mixture of different initial concentration for 30 min was sufficient to reach equilibrium. They also showed that increasing the initial cobalt concentration decreased cobalt removal percentage due to the saturation of clay sites with cobalt ions. Compared with the sorptions of cobalt to other bentonite and kaolinite [9,16], the sorption equilibration was reached quickly. The short time needed for adsorption to reach equilibrium could be attributed to the high adsorption efficiency of Saudi activated bentonite.

3.2. Effect of solution pH

Effect of solution pH on the removal of cobalt ions using Saudi activated bentonite was investigated in the solution pH range 1–10 with a constant clay amount of 0.5 g/50 mL of cobalt solution, a shaking time of 30 min and cobalt concentration of 50 mg/L. pH adjustments were carried out using 1 N HCl and 1 N NaOH, 200 rpm stirring rate and 25 ± 2 °C temperature was applied to the shaker. The results presented in Fig. 2 shows cobalt removal percentage at different solution pH. The lowest cobalt removal was found at pH 1. As the solution pH increased, cobalt removal percentage gradually increased up to pH 8. This may be attributed to the surface of Saudi bentonite which contains large number of active sites. Consequently, it may become positively charged at low pH, leading to increase the competition between H^+ and cobalt ions for available adsorption sites. However, as pH increases, this competition decreases as these surface active sites become more negatively charged, which enhances the adsorption of the positively charged metal ions through electrostatic force of attraction [17].

Increasing solution pH, cobalt removal percentage stays constant in the solution pH range 8–10, where the removal percentage was about 100%. This was due to the precipitation of $Co(OH)_2$ as reported before [9].

3.3. Effect of initial concentration

Fig. 3 shows the effect of initial cobalt concentration on cobalt removal when cobalt concentration varies from 25 to 200 mg/L under operating conditions of 30 min shaking time, 0.5 g of clay/50 mL for adsorbate and solution pH was kept constant at 7. The results showed a gradual decrease in cobalt removal

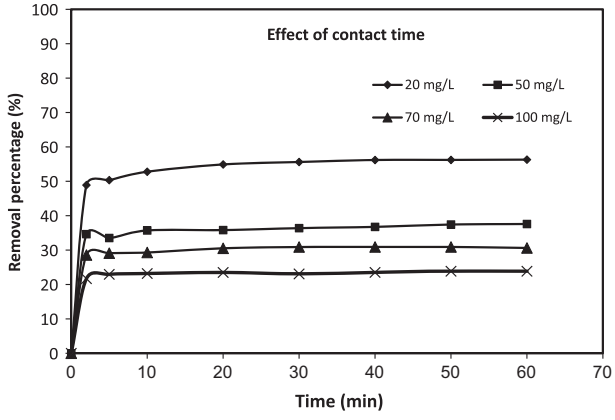

Figure 1 Effect of contact time on the removal of baltby Saudi Activated bentonite. Initial cobalt concentration varies between 20 and 100 mg/L, clay dosage: 0.5 g/50 ml, pH = 3.2.

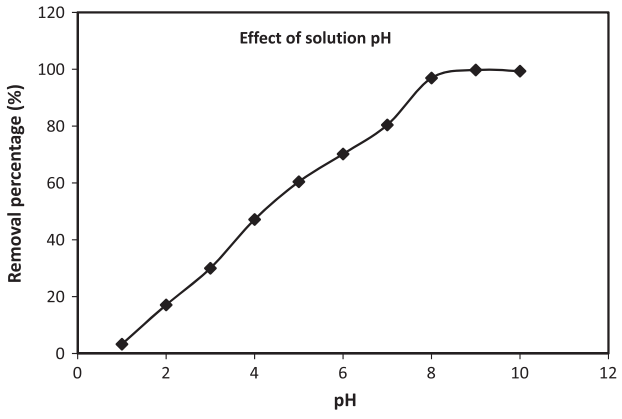

Figure 2 Effect of pH on the removal of cobalt by Saudi Activated Bentonite. Initial cobalt concentrations 50 mg/L, clay dosage: 0.5 g/50 mL, contact time: 30 min.

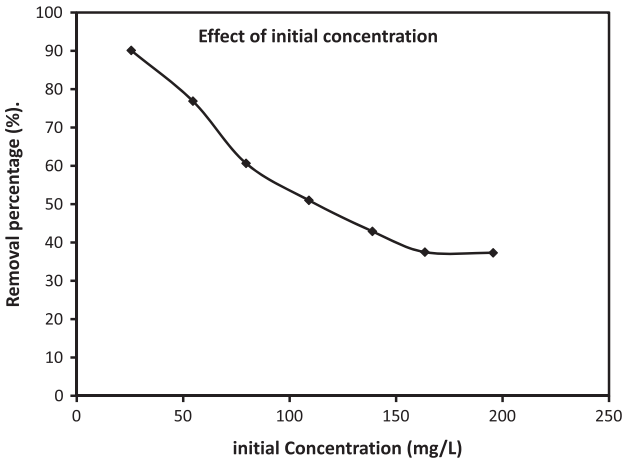

Figure 3 Effect of cobalt concentration on the removal of cobalt by Saudi activated bentonite. Clay dosage: 0.5 g/50 mL. pH = 7, contact time: 30 min.

when the cobalt concentration increased in the solution. The results also showed that about 90% of cobalt was removed when cobalt concentration was about 25 mg/L. Cobalt removal percentage decreases with increasing cobalt concentration to about 37% when cobalt concentration was 200 mg/L. This decrease was due to the fact that an increase in cobalt concentration makes a high ratio of the number of cobalt ions present in solution to the number of available adsorption sites [3].

3.4. Effect of clay dosage

The effect of the amount of Saudi activated bentonite (0.125–2.0 g/50 mL) on cobalt removal at constant values of initial metal concentration (50 mg/L), contact time (30 min), pH = 7 and temperature (25 ± 2 °C) is shown in Fig. 4. The results showed that the removal of cobalt increased gradually from 38% at 0.125 g/50 mL up to 100% at 1.0 g/50 mL. However, this result was expected since as the dose of adsorbent increases, the number of adsorbent sites increases. These amounts attach more ions to their surfaces [18]. When clay

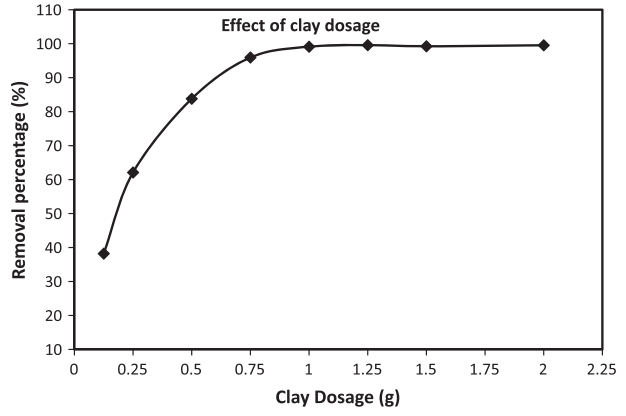

Figure 4 Effect of clay dosage on the removal of cobalt by Saudi activated bentonite. Initial cobalt concentrations 50 mg/L, pH = 7, contact time: 30 min.

dosage was increased to more than 1.0 g, the removal of cobalt was maintained constant at 100%. So, 1.0 g of activated bentonite was enough for the quantitative removal of cobalt from wastewater. Similar results were reported where many types of materials were used as adsorbents [19].

3.5. Adsorption isotherms

Adsorption isotherms of cobalt on Saudi activated bentonite were investigated using three different adsorption isotherm models, the Langmuir [20], Freundlich isotherm [21] and D–R [22] equations. These models were used to fit the experimental data obtained from this work. These models were tested to determine the maximal capacity of cobalt removal using Saudi activated bentonite. The quality of the isotherm fit to the experimental data was typically evaluated based on the magnitude of the correlation coefficient for the regression, i.e., the isotherm giving an R^2 value closest to unity is considered to give the best fit. The adsorption isotherms for cobalt removal were studied using different initial metal concentrations at adsorbent mass of 0.5 g at room temperature (25 °C) and solution pH7. Afterward, data obtained were fitted to the Langmuir, Freundlich and D–R isotherms.

The Langmuir isotherm was based on the assumption that it predicts monolayer coverage of the adsorbate on the outer surface of the adsorbent [20]. This model also suggests that there is no lateral interaction between the sorbed molecules.

The Langmuir equation, in the linear form is written as:

$$\frac{C_e}{q_e} = \frac{1}{bq_{\max}} + \frac{C_e}{q_{\max}} \tag{2}$$

where C_e is the equilibrium concentration of cobalt ions (mg/L); q_e is amount of cobalt ions adsorbed per unit weight of adsorbent (mg/g); $q_{\max}$ is amount maximum adsorption capacity (mg/g); b is the adsorption equilibrium constant (L/mg).

The data obtained from linear Langmuir isotherm plot for the adsorption of cobalt onto Saudi activated bentonite are presented in Table 2 and plotted in Fig. 5.

Table 2 The Langmuir, Freundlich and D-R equation parameters predicted from adsorption isotherm data of cobalt ions onto Saudi activated bentonite at pH = 7, 25 ± 2 °C and initial cobalt concentration of 50 mg/L.

Isotherm parameters	Values
Langmuir	
$q_{\max}$ (mg/g)	7.3
b (l/mg)	0.084
R^2	0.975
Freundlich	
K (mg/g)	2.33
n	4.5
R^2	0.936
D–R isotherm	
q_D (mg g^{-1})	6.6
B (mol^2 kJ^{-2})	6E-5
E (kJ mol^{-1})	91.3
R^2	0.75

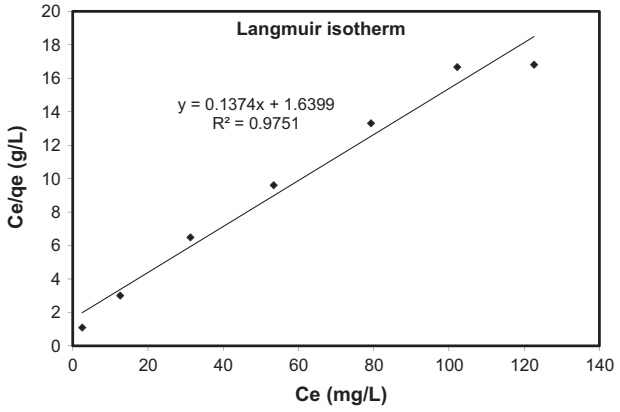

Figure 5 Langmuir plot for the adsorption of cobalt on Saudi activated bentonite. Clay dosage: 0.5 g/50 mL. pH = 7, contact time: 30 min.

The maximum adsorption (q_{max}) for cobalt on Saudi activated bentonite equals to 7.3 mg/g.

The Freundlich isotherm is based on multilayer adsorption on heterogeneous surface [21]. The linear form of Freundlich equation is written as:

$$\log q_e = \log K + \frac{1}{n}\log C_e \tag{3}$$

where k and n are the constant characteristics of the system.

The best estimated values of all the equation parameters are summarized in Table 2.

The applicability of the Freundlich adsorption isotherm was also analyzed, using the same set of experimental data, by plotting log (q_e) versus log (C_e). The data obtained from linear Freundlich isotherm plot for the adsorption of cobalt onto Saudi activated bentonite are presented in Table 2 and plotted in Fig. 6. The value of n between 1 and 10 shows a good adsorption which indicates that cobalt is favorably adsorbed by Saudi activated bentonite.

D–R isotherm is more general because it does not assume a homogenous surface or constant adsorption potential [22]. It was applied to estimate the porosity apparent free energy and the characteristics of adsorption. The linear form can be represented as:

$$\ln q_e = \ln q_D - B\varepsilon^2 \tag{4}$$

where B is a constant related to the mean free energy of adsorption (mol^2(kJ^2)$^{-1}$), q_D is the theoretical saturation capacity (mg/g), ε is the polyani potential, and is calculated as follows:

$$\varepsilon = RT\ln(1 + 1/C_e) \tag{5}$$

The slope of the plot of lnq_e versus ε^2 gives B and the intercept yields the adsorption capacity, q_D. The mean free energy of adsorption (E) (KJ mol^{-1}) is calculated from the equation:

$$E = 1/(2B)^{0.5} \tag{6}$$

The calculated value of D–R parameters is given in Table 2 and plotted in Fig. 7. The value of E calculated shows the process is chemisorptions since it was reported that physisorption processes usually have adsorption energies <40 kJ mol^{-1} and above this value sorption is of chemisorption mechanism [23]. Similar results were reported [24,25].

3.6. Adsorption kinetics

The kinetics of cobalt adsorption onto Saudi activated bentonite is required for selecting optimum operating conditions for the full-scale batch process. The kinetic parameters, which are helpful for the prediction of adsorption rate, give important information for designing and modeling the adsorption processes. Thus, the kinetics of cobalt adsorption onto Saudi activated bentonite was analyzed using pseudo-first-order, pseudo second-order. Moreover, the kinetics of sorption describing the solute uptake rate is one of the important characteristics defining the efficiency of sorption. The kinetic parameters for the adsorption process were studied on the batch adsorption at room temperature and pH at 3.2. The data were fitted to the first-order Lagergren equation [26],

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{7}$$

where k_1 is the first-order rate constant (min^{-1}); q_e is amount of adsorbed metal ions on bentonite at equilibrium (mg/g); q_t is

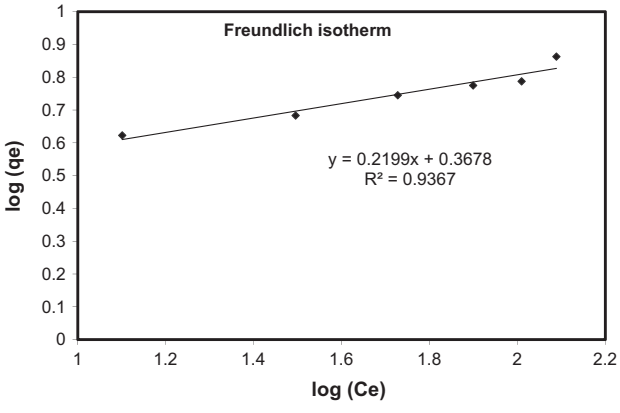

Figure 6 Freundlich plot for the adsorption of cobalt on Saudi activated bentonite. Clay dosage: 0.5 g/50 mL. pH = 7, contact time: 30 min.

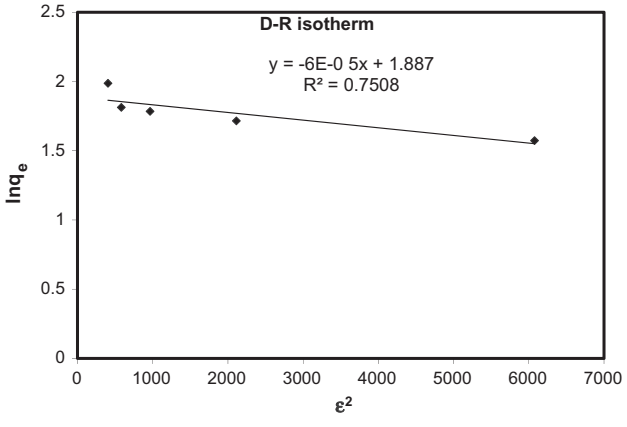

Figure 7 D–R plot for the adsorption of cobalt on Saudi activated bentonite. Clay dosage: 0.5 g/ 50 mL. pH = 7 , contact time: 30 min.

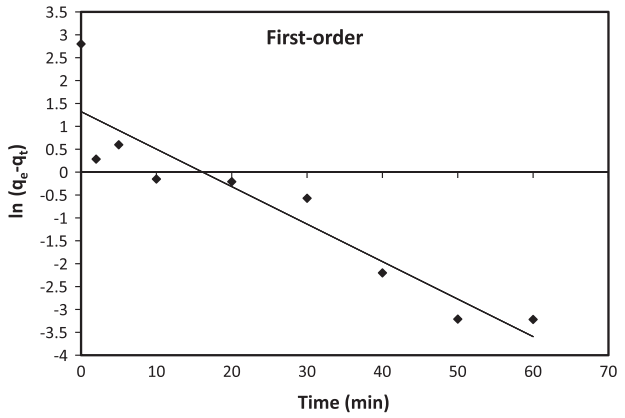

Figure 8 Plot of first order model for cobalt adsorption by Saudi activated bentonite. Initial cobalt concentration 50 mg/L, clay dosage: 0.5 g/50 mL, pH = 3.2.

the amount of cobalt adsorbed at time t (min) (mg/g).The first-order constants can be obtained by plotting log ($q_e - q_t$) versus time, as shown in Fig. 8.

The experimental adsorption kinetics data are analyzed by applying the pseudo-second-order kinetics model [27], which is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{8}$$

where k_2 is the pseudo-second-order kinetics constant (g/(mg/min)); q_e is amount of adsorbed metal ions on bentonite at equilibrium (mg/g); q_t is the amount of cobalt adsorbed at time t (min) (mg/g).

The fit of this model was checked by each linear plot of (t/q_t) versus t as shown in Fig. 9.

By comparing regression coefficients for each expression, a good agreement of the experimental data with the second order kinetic model was observed for cobalt adsorption onto Saudi activated bentonite. The correlation coefficient for the second order kinetic model for cobalt adsorption was around 1.0. Thus, a plot of t/q_t against t should give a linear relationship with a slope of $1/q_e$.

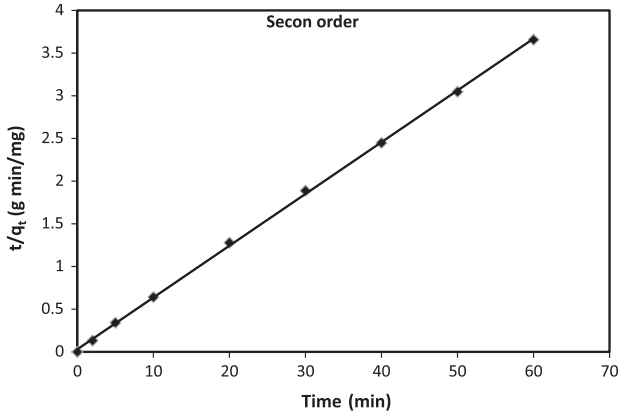

Figure 9 Plot of second order model for cobalt adsorption by Saudi activated bentonite. Initial cobalt concentration 50 mg/L, clay dosage: 0.5 g/50 mL, pH = 3.2.

4. Conclusion

The interaction of cobalt ions with Saudi activated bentonite from Khulays bentonite deposit: 95 km north of Jeddah was investigated under various conditions. The results obtained from this study are summarized below.

- Adsorption of cobalt ions on Saudi activated clay was relatively fast and the equilibrium was reached after 30 min. The results showed that shaking the mixture of different initial concentration for 30 min was sufficient to reach equilibrium.
- They also showed that increasing the initial cobalt concentration decreased cobalt removal percentage due to the saturation of clay with cobalt ions.
- Cobalt removal percentage gradually increased with increasing solution pH up to pH 8. This may be attributed to the surface of Saudi bentonite which contains large number of active sites. Further, increase in solution pH cobalt removal was kept constant in the solution pH range 8–10, where the removal percentage was about 100%.
- Cobalt removal decreased with increasing cobalt concentration when cobalt concentration increased from 20 to 100 mg/L. The removal of cobalt increased as the dose of Saudi activated bentonite increased. This was due to increase in the number of adsorbent sites.
- The adsorption isotherm data were well fitted with both the linearized Langmuir and Freundlich isotherm. Furthermore, the value of the mean free energy determined with the D–R equation showed that adsorption process is chemisorptions.
- A batch adsorption kinetic experiment revealed that cobalt adsorption onto Saudi activated bentonite is well represented by the pseudo-second-order kinetic model. It can be concluded that film diffusion and intraparticle diffusion are simultaneously operating in the whole adsorption process. Saudi activated bentonite can be considered as a promising adsorbent for the removal of cobalt from aqueous solutions.

Acknowledgements

The author would like to thank the Deanship of Scientific Research, King Abdulaziz University, for their financial support to accomplish this study. He would also like to thank Department of Chemical Engineering staff, King Abdulaziz University, for their continual support and invaluable suggestions during this research project.

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